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THE ADAPTATION OF THE GOLD AMALGAMATION SAMPLING AND ANALYTICAL PROCEDURE FOR THE ANALYSIS OF MERCURY IN STACK CASES TO HIGH SO_2 ENVIRONMENTS OBSERVED IN SMELTERS

by

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for

The ENVIRONMENTAL PROTECTION AGENCY
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16. Abstracts *The objective was the adaption of the gold amalgamation sampling procedure for the collection of mercury in gas streams having high SO_2 concentrations. This method consists of removing volatile mercury from the gas stream by amalgamating it on gold foil. The gold amalgam sampling and analytical procedure developed for power plants was directly amenable to the zinc smelter investigated. SO_2 concentrations as high as 7.5% did not effect the sampling and analytical procedure. When using a stannous chloride or distilled water scrubber during one minute runs over a wide range of flow rates reproducible results were obtained with a 95% plus recovery on the first amalgamator. The stability of the mercury-gold amalgam depends on the temperature of the gas stream. The major problem was the high sensitivity of the analytical procedure resulting in a very short sampling period.*

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INTRODUCTION

A cross-section of copper, zinc and lead sulfide ores from the United States have been analyzed for mercury showing a range of < 0.05 to 300 ppm.[1,2] In the initial smelting operation these ores are roasted to volatilize the sulfur and produce the oxide (calcine) of the heavy metals. The sulfur, volatilized as SO_2, is either released to the atmosphere or collected as sulfuric acid in an acid recovery plant. During this stage of the smelting operation a large percentage of the mercury present in the ore is volatilized. This mercury is either released to the atmosphere or is entrapped in the acid recovery plant.

Initial efforts to analyze the gas stream from the roaster for mercury have utilized an ICl wet oxidizing isokinetic sampling train.[3] The high SO_2 concentrations (as high as 7.5%) in the gas stream reduces the ICl almost instantaneously, eliminating the oxidizing capability of the solution. This immediate loss of oxidizing capability also occurs with an acidic-permanganate sampling train. Because of the inability of these liquid trains to maintain their oxidizing power during the sampling period an alternate method of collection of mercury from the effluent gas stream is needed.

The objective of this study is the adaption of the gold amalgamation sampling procedure[4] for the collection of mercury in gas streams having high SO_2 concentrations. This method, developed under Phase I of this

contract, consists of removing volatile mercury from the gas stream by amalgamating it on gold foil. Two modified Smith-Greenburg impingers from a standard EPA sampling train are altered to support approximately 10 grams of gold foil chips. The sample is collected by a method similar to the particulate procedure as designated in the Federal Register.[5] The amalgamators (modified impingers containing gold chips) are fired in an induction furnace revolatilizing the mercury which is carried by an air stream through a quartz cell in an atomic absorption spectrophotometer (flameless atomic absorption). The mercury concentrations are calculated from the peak heights observed on the strip chart recording of the spectrophotometer at the 254 mμ absorption line utilizing a standard analytical curve prepared with standard solutions. Standards are run after each stack sample by aerating reduced mercury from a standard solution onto the gold foil chips and then revolatilizing it with the induction furnace into the quartz optical cell. Because of the lack of wet chemicals in the system there is no blank determination as required with the liquid oxidizing sampling trains.

SAMPLING SITE

The plant utilized in this study was the American Smelting and Refining Company (ASARCO) zinc smelter in Columbus, Ohio. A flow chart of the initial smelting process at this plant is presented in Figure 1. The ore is roasted at 900°C volatilizing the sulfur as SO_2, and the mercury,

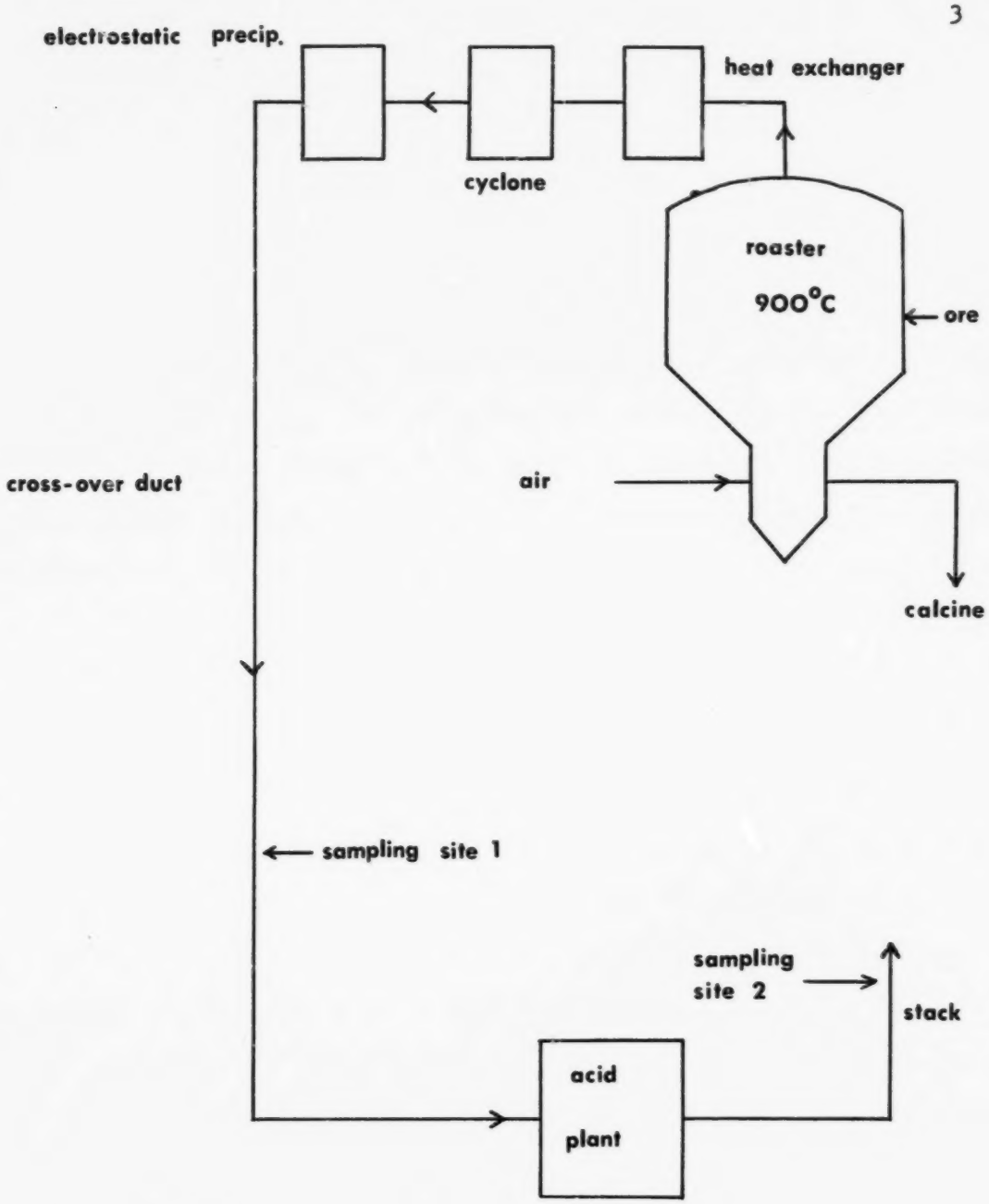

Figure 1. Flow Chart of the Initial Smelting Process at the ASARCO Columbus, Ohio Zinc Smelter

presumably, as elemental mercury (essentially no organic material is present in the ore eliminating the possibility of a volatile organo-mercury compound). Particulates are removed from the gas stream by a cyclone and two electrostatic precipitators. The effluent gas stream is carried through a 3½ foot diameter stainless steel duct to the acid recovery plant where the SO_2 is removed as sulfuric acid.

The zinc ore (concentrate) is from Mascot, Tennessee. Analyses of the zinc concentrate and calcine as provided by ASARCO is:

Milled Zinc Concentrate		Zinc Calcine (Lurgi)	
Zn	60 - 63%	Zn	70 - 73%
S	31 - 33%	S	1½ - 2½%
Fe	1 - 2%	Sulfide S	0.5 - 0.8%
Cd	0.3%	Cd	0.4%
Pb	0.01%		

Mercury concentrations of the milled zinc concentrate and the zinc calcine as determined from grab samples by the authors utilizing a combustion-digestion procedure followed by flameless atomic absorption were:

	Concentrate	Calcine (Lurgi)
5/11/72	0.86 ppm	
5/25/72	1.1 ppm	0.45 ppm

Utilization of these values for a mass balance is difficult since the calcine represents unknown proportions from the roaster, heat exchanger, cyclone, and electrostatic precipitators.

The effluent gas stream contains approximately 7.5% SO_2 and has a flow rate between 12,000 and 15,000 CFM(figures provided by ASARCO and EPA).

The milled concentrate, as fed to the roaster, has a 0.5% moisture content. Based on this figure and the average relative humidity, the effluent gas stream would contain between 1 and 2% moisture.

The primary sampling site was located in the horizontal cross-over duct between the roaster and the acid recovery plant. The port was in a 3½ foot diameter duct about 60 feet above ground level. This duct contains a 150 foot straight section (no constrictions or bends) and the sampling site was located 30 feet from the downstream end presenting ideal isokinetic sampling conditions. A single 4 inch diameter port was constructed. The flow in this duct was controlled by an ID and an FD fan resulting in a positive-negative interface that migrated back and forth along the duct creating some sampling problems. A secondary site, constructed by Battelle on the acid recovery plant stack, was utilized for two runs.

THEORETICAL MASS BALANCE

A theoretical mass balance, based on a 200 ton daily concentrate consumption, was calculated to predict an approximate mercury concentration in the cross-over duct. These calculations are based on a 1.0 ppm average mercury concentration in the ore and the assumption that all the mercury is volatilized during the roasting operation.

Plant Consumption:	200 tons concentrate/day
Mercury Concentration:	1.0 ppm
Air Flow:	12,000 - 15,000 CFM

200 tons/day = 400,000 lbs./day = 277 lbs./min.

1.0 ppm = 0.000001 gms. Hg/gm. ore

277 lbs./min. x 454 gms./lb. = 125,758 gms./min.

125,758 gms./min. x 0.000001 gms. Hg/gm. ore = 0.126 gms. Hg/min.

12,000 CFM x 0.0283 M^3/CF = 340 M^3/min.

0.126 gms. Hg/min. / 340 M^3/min. = 0.000371 gms. Hg/M^3

= 371 $\mu g/M^3$ Hg in effluent gas

This value represents the maximum concentration obtainable based on the complete volatilization of all the mercury during combustion. Recalculating these results, correcting for the calcine concentration that is not volatilized, we obtain:

Volatile mercury lost during roasting = 1.1 - 0.45 = 0.55 ppm

0.55 / 1.1 = 50% of total mercury volatilized during roasting

0.50 x 371 μg Hg/M^3 = 186 $\mu g/M^3$ Hg in effluent gas stream

These parameters are calculated at stack conditions (pressure and temperature) and would result in higher concentrations when monitored at the sampling gas meter pressure and temperature.

SAMPLING PROCEDURE

The general procedure used was based on the method developed for mercury in power plant stacks as determined in Phase I of this study. Gold foil, based on its ability to quantitatively absorb mercury from a gas stream by an amalgamation reaction, was used to collect the mercury. Modified

Smith-Greenburg impingers were altered by forming a three finger support in the center to support a 2 gram gold wire plug and 8 to 10 grams of gold foil chips, 0.004 inches thick. A 28/15 pyrex ball joint was attached to the bottom of the modified impinger. This unit, called an amalgamator, was inserted into the standard EPA isokinetic sampling train. The completed sampling train contained a fiber glass filter and a cyclone heated to 200°F. A five foot glass probe with a 0.250 inch diameter nozzle was operated at 150°F. Five or six impingers were used in the train: the first impinger contained a scrubber solution, the second was empty (collected entrained water), the third and fourth were gold amalgamators, the fifth contained a 10% H_2O_2 solution to collect SO_2 (a 7½% SO_2 concentration is detrimental to the equipment), and the final impinger contained silica gel to remove water vapor.

After the mercury has been amalgamated from the gas stream, 0.5 cubic feet of ambient air is pulled through the impingers to volatilize any ground state elemental mercury in the scrubber solution. After the amalgamator is removed from the sampling train it is placed in an induction furnace. Air is passed through the amalgamator at a constant flow rate (1.4 liters/min.) by connecting a metered air line to the amalgamator with ball joints. The induction furnace is fired at a 100% setting and the air stream carries the revolatilized mercury through a 3 inch long quartz optical cell in the optical path of the spectrophotometer. The absorption is measured as the peak height in percent absorption on a strip chart recorder. Standards are run after each stack sample by

placing an aliquot of a standard solution in an aeration cell located in the air line prior to the amalgamator. This standard mercury solution is reduced (1 ml. 20% $SnCl_2$ in 50% conc. HCl) and aerated (1.4 liters air/min.), volatilizing the mercury which is collected on the amalgam. The amalgam is then fired in the induction furnace and analyzed by a procedure identical to that used for the amalgamated stack sample. Previous work by the authors[4] have shown that the shape of the standard peak more closely approximates the sample peak if the standard is amalgamated by flow down through the gold (the same direction as the air flow in the isokinetic train). All standards run in this study were done by this method requiring the additional step of reversing the air flow through the amalgamator while amalgamating the the standard.

The specific parameters investigated or optimized in this investigation were:

1- Sampling Time

The amount of time in which the sample is collected is determined by the mercury concentration in the gas stream being investigated. The sensitivity of the analytical procedure limits the sample size to approximately less than 2 μg mercury. This results in shorter sampling periods at higher stack gas mercury concentrations.

2- Interferences

Previous work at power plants[4] suggested that sulfuric acid mist condenses on the gold and breaks down when fired in the induction furnace releasing water vapor which also absorbs 254 mμ radiation. This phenomena is observed as a prepeak

before the mercury peak and contains a non-reproducible peak height. Various scrubber solutions in the first impinger have been investigated as possible means of eliminating this interference. Specifically, a 1½ % stannous chloride solution in 4% hydrochloric acid or distilled water greatly reduces this interference even at high SO_2 concentrations. The stannous chloride solution was used to maintain a reducing environment, thus reducing the mercury retention of the solution. Previous work has shown that the mercury retention is about the same for both types of scrubbers. This could be related to the reducing capability of the SO_2. The utilization of either of the scrubber solutions will require an additional mercury determination on the solution. During this study samples were collected with (1) a stannous chloride scrubber, (2) a distilled water scrubber, and (3) a dry impinger (no scrubber solution).

3- Gold Deterioration

The gold utilized in power plant studies required refiring in an oven at 750°C after each use in the stack. Lower, broader peaks and poorer recoveries were obtained when the gold was not fired. It is felt that this is a function of the absorption or condensation of hydrocarbons on the gold. The absence of hydrocarbons in the combustion process of a smelter should eliminate or greatly decrease this problem.

4- Mercury Concentration as a Function of Flow Rate (CFM)

A series of runs were performed to determine if there is any difference in collection efficiencies at different sampling rates (CFM).

5- Efficiency of Recovery

The efficiency of the amalgamation of the mercury on the first amalgamator was investigated as a function of the total amount collected on both amalgamators.

6- Isokinetic Sampling

As a means of controlling the parameters for optimization of the procedure, most of the sampling runs were performed non-isokinetically. Three runs were performed isokinetically, collecting samples of the scrubber, probe and cyclone wash, and the filter. Due to the high mercury concentrations observed in the stack gas, the runs were of a one minute duration, precluding changing ΔH during the collection period. Therefore, all the runs were done at a constant sampling rate. The scrubber and wash solutions were analyzed by a stannous chloride reduction - flameless atomic absorption procedure. The mercury in the filter paper particulate samples was volatilized by combustion in the induction furnace and then collection in an acidic oxidizing solution (30 ml. 3% $KMnO_4$ and 10 ml. conc. HNO_3). This solution was reduced, aerated, and then analyzed by flameless atomic absorption.

7- Zinc-Mercury Amalgam

The roasting of the zinc ores may result in a relatively high concentration of volatile and particulate zinc in the gas stream.

The volatile mercury in the gas stream could be amalgamated with the zinc. If this potential amalgam was not retained by the filter it is unknown if it would react with the gold. Due to the temperature of the gas stream (450 - 480°F) it is highly unlikely that a zinc-mercury amalgam would form or be stable. As a precautionary measure the hydrogen peroxide scrubber was analyzed for mercury and zinc during one day's runs.

RESULTS

The observed mercury concentrations and the control parameters are presented in Tables 1 and 2 as a daily log of the runs. The volumes collected and the results of the isokinetic runs are presented in Table 3. The results of the combined zinc and mercury analyses obtained on the scrubber solutions of May 26 are presented in Table 4. The results will be interpreted in relation to the parameters discussed in the previous section: sampling time, interferences, gold deterioration, mercury concentration as a function of flow rate, efficiency of recovery, isokinetic sampling, and zinc-mercury amalgams.

1- Sampling Time

Initial sampling periods of 5 and 10 minutes resulted in peak heights in excess of 90% absorption. These peaks were too high to be interpreted quantitatively, resulting in the final acceptance of one minute runs. Samples collected at 0.4 CFM or higher rates during one minute sampling periods contained in excess of 3 µg of mercury and resulted in 85 to 90% absorption. These absorptions are too high for accurate

Table 1. Daily Log of Runs: Mercury Concentrations and Control Parameters

DATE	TIME	SAMPLING TIME	SAMPLING RATE	GAS VOLUME	IMPINGER ORDER	MERCURY				AMAL. #1 % RECOVERY
						AMAL. #1	AMAL. #2	TOTAL	CONCENTRATION	
		minutes	CFM	liters		µg	µg	µg	µg/l.	
5/22/72	3:23	10	0.446	126	AAOE	~0.7	~3	~3.7	~0.03	19%
	4:30	10	0.461	130	SEAO	>10		>10		
	4:55	10	0.503	142	SEAO	>10		>10		
	5:20	10	0.472	133	HEAO	>10		>10		
	5:39	10	0.458	130	SEAO	~25		~25	~0.19	
5/23/72	9:50	5	0.450	63.5	SEAAO	~10	5.05	~15	~0.24	66%
	10:15	5	0.455	64.2	SEAAO	~10	1.88	~11.9	~0.19	84%
	10:40	5	0.457	64.5	SEAAO	~10	~3	~13	~0.20	77%
	11:03	2	0.471	26.7	SEAAO	2.2	3.8	6.0	0.22	58%
	11:20	1	0.460	13.0	SEAAO	1.3	0.9	2.2	0.17	59%
	11:45	2	0.462	26.1	SEAAO	5.1	0.52	5.6	0.21	91%
	1:30	1	0.454	12.8	SEAAO	1.8	0.41	2.2	0.17	82%
	2:54	1	0.476	13.5	SEAAO	1.6	1.8	3.4	0.25	47%
	3:15	1	0.483	13.7		1.0	1.7	2.7	0.20	37%
		1	0.465	13.1		~3	0.17	3.2	0.24	94%
5/24/72	8:39	1	0.477	13.5	SEAAO	3.2	0.10	3.3	0.24	97%
	8:55	1	0.449	12.7	SEAAO	3.9	0.12	4.0	0.31	97%
	9:13	2	0.488	27.6	SEAAO	5.0	1.1	6.1	0.22	82%
	9:31	1	0.492	13.9	SEAAO	3.2	0.08	3.3	0.24	97%
	9:55	1	0.503	14.2	SEAAO	3.0	0.22	3.2	0.23	94%
	10:19	1	0.502	14.2	SEAAO	2.0	1.1	3.1	0.22	63%
	11:19	1	0.500	14.1	HEAAO	1.1	0.97	2.1	0.15	52%
	11:41	1	0.528	15.0	HEAAO	3.1	0.10	3.2	0.21	97%
	12:17	1	0.510	14.4	HEAAO	3.2	0.10	3.3	0.23	97%
	1:00	1	0.499	14.1	HEAAO	2.9	0.9	3.8	0.27	76%
	1:16	1	0.557	15.8	EEAAO	1.1	2.5	3.6	0.23	31%

DATE	TIME	SAMPLING TIME	SAMPLING RATE	GAS VOLUME	IMPINGER ORDER	MERCURY				AMAL. #1 RECOVERY
						AMAL. #1	AMAL. #2	TOTAL	CONCENTRATION	
		minutes	CFM	liters		µg	µg	µg	µg/l.	
5/25/72	10:39	1	0.464	13.1	HEAAO	3.1	0.15	3.3	0.25	94%
	10:55	1	0.454	12.8	HEAAO	3.8	0.09	3.9	0.30	97%
	11:39	1	0.477	13.5	HEAAO	4.1	0.42	4.5	0.33	91%
	2:40	1	0.548	15.5	HEAAO	3.3	0.06	3.4	0.22	97%
	3:33	1	0.560	15.9	HEAAO	2.7	1.4	4.1	0.26	66%
	4:58	1	0.504	14.3	HEAAO	3.1	0.2	3.3	0.23	94%
	5:35	1	0.575	16.3	HEAAO	4.1	0.06	4.2	0.26	98%
	5:47	1	0.674	19.1	HEAAO	5.0	0.16	5.2	0.27	96%
5/26/72	9:43	1	0.594	16.8	HEAAO	2.7	0.04	2.7	0.16	99%
	10:03	1	0.324	9.2	HEAAO	2.4	0.18	2.6	0.28	92%
	10:24	1	0.449	12.7	HEAAO	3.6	0.18	3.8	0.30	95%
	10:50	1	0.648	18.3	HEAAO	4.9	0.24	5.1	0.28	96%
	11:35	1	0.810	22.9	HEAAO	6.3	0.95	7.2	0.31	88%
	12:15	1	0.226	6.4	HEAAO	1.5	0.45	2.0	0.31	75%
	2:05	1	0.800	22.6	HEAAO	5.0	0.80	5.8	0.26	86%
	2:45	1	0.280	7.9	HEAAO	1.7	0.36	2.1	0.27	81%
	4:30	1	0.690	19.5	AAEO	2.6	1.2	3.8	0.19	68%
	4:47	1	0.684	19.3	AAEO	2.2	1.1	3.3	0.17	67%
					Acid Recovery Plant Stack					
		5	0.570	80.7	HEAAO	0.01	0.01	0.01	0.0001	-
		20	0.577	327	HEAAO	0.48	0.35	0.83	0.0025	58%

Impinger Order: A - gold
E - empty
H - water scrubber
S - $SnCl_2$ scrubber
O - peroxide scrubber

Table 2. Daily Log of Runs: Control Parameters

DATE	TIME	DRY GAS TEMP.	AMALGAMATOR	GOLD		STACK CONDITIONS			INSTRUMENT PARAMETERS			PROBE TIP DIRECTION
				CONDITION	AMOUNT	STATIC PRESSURE	ΔP	TEMP.	AIR-FLOW Perkin-Elmer Units	CELL SIZE inches	FIRING TEMP. %	
		°F	mm.		grams	" H_2O	" H_2O	°F				
5/22/72	3:23	85	15	F	10	-0.40		445	3	3"	100%	Down
	4:30	87		F		---		450				
	4:55	87				-0.39		455				
	5:20	87				-0.42		460				
	5:39	88				-0.43		460				
5/23/72	9:50	78	15	F	10	-0.38		455	3	3"	100%	Down
	10:15	80		F		-0.30		460				
	10:40	81				-0.29		455				
	11:03	82				-0.29		450				
	11:20	-				-0.33		450				
	11:45	82				-0.35		445				
	1:30	-				-		460				
	2:54	-				-		465				
	3:15	-				-		460				
	---	-				-0.40		465				
5/24/72	8:39	-	15	F	10	-0.54		480	3	3"	100%	Down
	8:55	-		F		-0.54		475				
	9:13	78				-0.57		480				
	9:31	-				-0.53		485				
	9:55	-				-0.52		485				
	10:19	-				-0.51		490				
	11:19	-				-0.46		475				
	11:41	-				-0.48		470				
	12:17	-				-0.51		470				
	1:00	85				-0.54		480				
	1:16	-				-0.52		480				

DATE	TIME	DRY GAS TEMP.	AMALGAMATOR	GOLD		STACK CONDITIONS			INSTRUMENT PARAMETERS			PROBE TIP DIRECTION
				CONDITION	AMOUNT	STATIC PRESSURE	ΔP	TEMP.	AIR-FLOW Perkin-Elmer Units	CELL SIZE	FIRING TEMP.	
		°F	mm.		grams	" H_2O	" H_2O	°F		inches	%	
5/25/72	10:39	-	15	F	10	-0.31	0.43	480	3	3"	100%	Up
	10:55	-		F		neg.	0.42	480				
	11:39	-				neg.	0.42	475				
	2:40	-				pos.	0.50	475				
	3:33	-				pos.	0.50	475				
	4:58	87				neg.	0.48	475				
	5:35	-				neg.	0.50	455				
	5:47	-				neg.	0.50	435				
5/26/72	9:43	68	15	F	10	-1.4	0.44	405	3	3"	100%	Up
	10:03	-		F			0.43	390				
	10:24	-					0.44	420				
	10:50	72					0.50	455				
	11:35	74					0.53	450				
	12:15	-					0.51	455				
	2:05	-					0.44	475				
	2:45	-					0.44	480				
	4:30	-		F			0.46	470				
	4:47	-					0.49	470				
					Acid Recovery Plant Stack							
5/26/72	-	-	15	F	10	-0.15		169	3	3"	100%	Up
	-	-						170				

Gold Condition: F - fired at 750°C
- not fired

analytical interpretation, but shorter sampling periods would have resulted in more erratic data due to the effect of the dead space of the sampling train (probe, cyclone, filter, impinger and embilical hose volume).

2- Interferences

The prepeaks and soluble white precipitate observed at the fossil fuel fired power plants did not occur at the smelter. It was suggested by the authors[4] that this phenomenon was related to the sulfuric acid mist concentration of the power plants. The low moisture content of the smelter gas stream would have lowered the percentage of sulfuric acid mist, but the higher SO_2 concentrations could have resulted in a greater total amount. The absence of this phenomenon may be partially attributed to the short sampling periods.

Samples were collected with stannous chloride solution and distilled water scrubbers as well as without a scrubber. These solutions were originally designed as an aid in eliminating the sulfuric acid mist. At this site the scrubbers had no apparent effect on the sulfuric acid mist due to its apparent absence at concentrations influencing the analyses. The scrubber solutions did effect the efficiency of recovery of the mercury on the first amalgamator. As has been suggested by the authors[4] (Phase I of this study) and by Diehl, etc.[6] the stability of the mercury amalgam in an air stream is temperature dependent. Hot air streams tend to 'leach' the mercury off the amalgam over an extended period. This would be illustrated by a lower percent recovery on the first amalgamator when a scrubber is not used

(less cooling of the gas stream) and by a lower percent recovery during extended sampling periods. The four samples collected without a scrubber solution showed a considerably lower percent recovery than the norm: 19%, 31%, 68%, and 67%. The five ten minute runs on May 22 illustrate the differences observed when a scrubber is not used. With the gold in the first impinger (no empty ice cooled impingers to lower the temperature) the recovery on the first amalgamator was 19%, and the total amount collected was much lower than actually existed. The remaining four runs contained the amalgamator in the third impinger position with a scrubber solution in the first position. In each case the total amount recovered approximated the values obtained in the later one minute runs. These four runs utilizing a scrubber also had a high recovery ratio on the first amalgamator. The 20 minute sample collected at the acid recovery plant showed only a 58% recovery when a water scrubber was used and did contain a small prepeak. From these results it is suggested that longer sampling periods will result in quantitative (95% +) amalgamation on the first amalgamator, but this will be accompanied by a slow revolatilization of the mercury off this amalgam onto the second amalgamator as the system slowly heats. With extended sampling periods this may result in the necessity of using three amalgamators.

There were no differences observed between the distilled water and the stannous chloride solution scrubbers resulting in the usage of distilled water in most of the runs. When performing isokinetic source sampling the scrubber solution should be combined with the probe and cyclone wash solutions for analyses.

3- Gold Deterioration

Gold deterioration was not a major problem at this site. Four batches of gold were rotated through the amalgamators and were cleaned by firing at 750°C at the completion of each day's runs. Minor deterioration was observed as a slight loss in sensitivity during the last few runs of each day. An example of this was observed in the results obtained on May 24 where a 3 µg standard deteriorated from 81% absorption to 73% absorption over the course of the day. This lack of gold deterioration may be related to short sampling periods, but it is felt by the authors that this is a function of the absence of hydrocarbons in the system.

4- Mercury Concentration as a Function of Flow Rate (CFM)

Figure 2, containing the data from samples collected and analyzed on May 26, graphically illustrates the lack of dependence of the amalgamation reaction on flow rate.

5- Efficiency of Recovery

With optimum sampling procedures and a scrubber solution to lower the gas temperature, 95% plus recovery was obtained with a one minute run. Lower percent recoveries on the first amalgamator were observed during 2, 5, and 10 minute sampling periods and when a wet scrubber was not used before the amalgamators in the train.

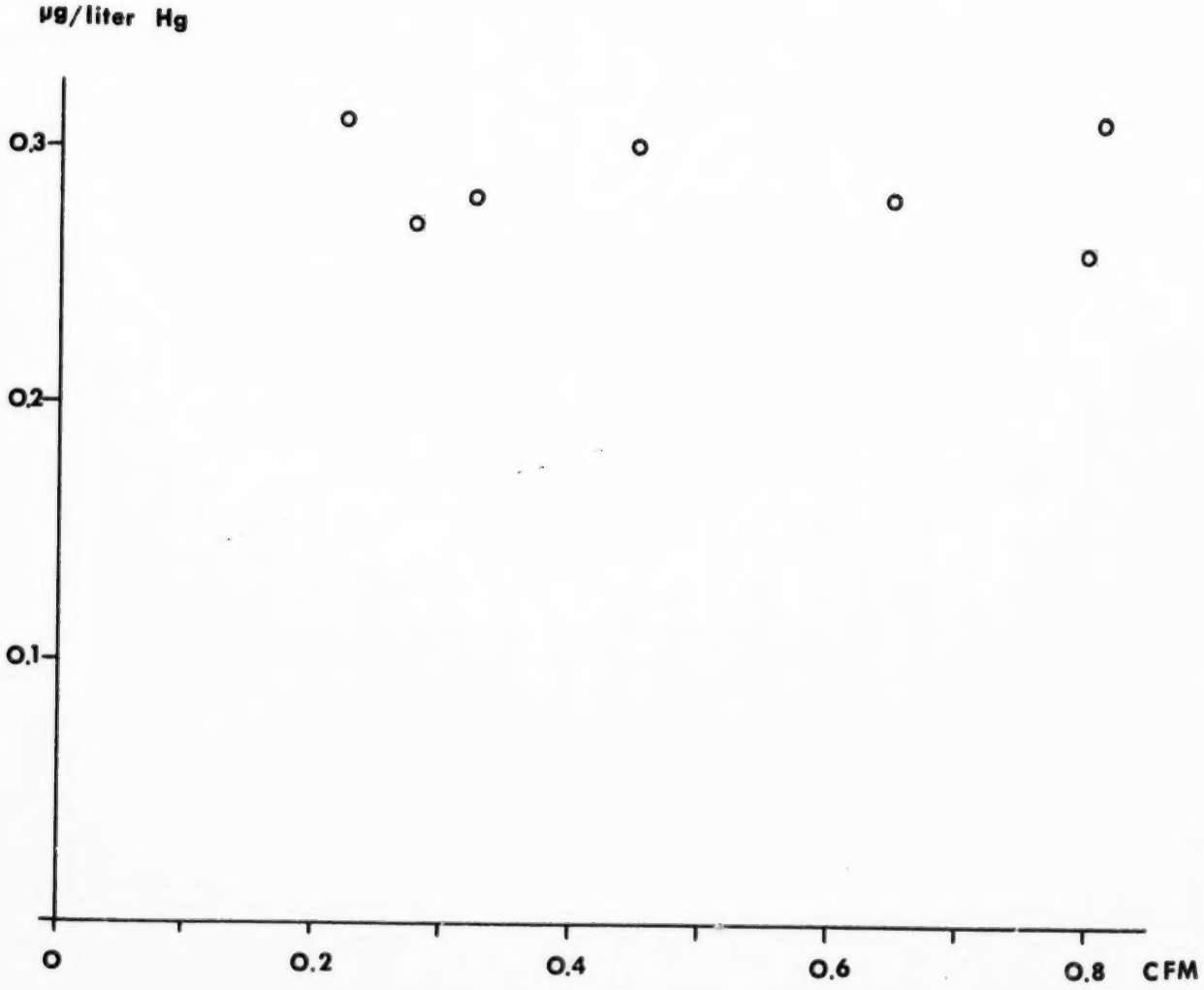

Figure 2. Mercury Concentration as a Function of Sampling Rate (CFM)

6- Isokinetic Sampling

The samples obtained isokinetically were runs 4, 5 and 6 on May 25. The results are presented in Table 3. These samples were obtained with a one minute sampling period, reducing the significance of an isokinetic sample. Problems were encountered with the filter paper analyses due to the breakage of the quartz combustion crucibles. The induction furnace melted the fiber glass and when it cooled, the quartz crucibles broke from the differential thermal contraction. Because of this mercury concentrations on the blank filters were not determined.

7- Zinc-Mercury Amalgam

The results of the analyses of the scrubber solutions collected on May 26 are presented in Table 4. The limited data shows a weak correlation between the mercury and zinc concentrations in the peroxide solutions. With one exception, insignificant amounts of mercury were observed in the peroxide solutions suggesting that the double amalgamators have quantitatively removed the mercury from the air stream.

The one high mercury concentration observed in the peroxide solutions does correspond with a high zinc concentration suggesting the possible presence of a zinc amalgam. (This value also corresponds to the highest stack gas temperature observed on May 26 and the highest sampling rate, 0.800 CFM.) The high sampling rate in conjunction with the high stack gas temperature may be separately influencing the collection efficiencies of the mercury and zinc.

Table 3. Results of Isokinetic Studies

DATE	TIME	WASH and SCRUBBER SOLUTION	MERCURY					
			AMAL. #1	AMAL. #2	FILTER	WASH and SCRUBBER SOLUTION	TOTAL	CONCENTRATION
		ml.	µg	µg	µg	µg	µg	µg/liter
5/25/72	2:40	136	3.3	0.06	0.43	0.14	3.9	0.25
	3:33	179	2.7	1.4	0.38	0.04	4.5	0.28
	4:58	246	3.1	0.20	---	0.49	(3.7)	0.26

Table 4. Mercury and Zinc Analyses of Scrubber Solutions

DATE	TIME	SAMPLING RATE	H_2O SCRUBBER		H_2O_2 SCRUBBER		
			SOLUTION	ZINC	SOLUTION	ZINC	MERCURY
		CFM	ml.	µg	ml.	µg	µg
5/26/72	9:43	0.594	265	31.8	247	146	0.14
	10:03	0.324	265	74	98	15	0.14
	10:24	0.449	265	45	104	51	0.24
	10:50	0.648	260	39	99	26	0.08
	11:35	0.810	256	87	96	29	0.22
	12:15	0.226	264	26	99	26	---
	2:05	0.800	252	32	98	380	1.5
	2:45	0.280	251	24	100	18	---

The similarity of the results obtained with the amalgamators over the wide range of sampling rates used on May 25 and 26 (probe tip pointed upstream) and May 22, 23, and 24 (probe tip pointed downstream) suggests that if a zinc-mercury amalgam does exist at 450°F it is either (1) collected on the fiber glass filter, (2) of a gaseous and not a particulate nature, or (3) does not interact with the gold, forming an amalgam.

CONCLUSIONS

The gold amalgam sampling and analytical procedure developed for power plants was directly amenable to the zinc smelter investigated. SO_2 concentrations as high as 7.5% did not effect the sampling and analytical procedure (corrosive effect on sampling equipment is unknown at this time). When using a stannous chloride or distilled water scrubber during one minute runs over a wide range of flow rates reproducible results were obtained with a 95% plus recovery on the first amalgamator.

The most significant accomplishment of this study was the realization of the dependency of the stability of the mercury-gold amalgam on the temperature of the gas stream. The leaching of the mercury off the amalgam by a stream of hot air, previously suggested by the authors, was illustrated in this study by the four runs containing no scrubber solutions and by the longer 20 minute run at the acid plant stack. If longer sampling times are to be utilized, future studies should consider the use of three amalgamators in series and/or additional cooling of the impingers.

The major problem encountered in this investigation was the high

sensitivity of the analytical procedure resulting in a very short sampling period. This problem may be solved by firing the gold amalgam into an acidic oxidizing solution and then analyzing aliquots of the solution. Additional methods of desensitizing the analytical procedure were outlined in the final report of Phase I of this study[4] and would be applicable to smelters. The sensitivity problem becomes more critical in consideration of the fact that the ore utilized at this smelter has a low mercury concentration compared to most sulfide ores in this country.

The results of the zinc-mercury amalgam study were inconclusive. Most of the zinc in the system is present as the oxide which should not form an amalgam with the volatile mercury. Based on this fact and the results of the study, it is very questionable that the amalgam exists at a concentration high enough to influence the results.

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